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N64-15866 (mf)

code 1  
CR 55740

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**ELECTRONIC RESEARCH DIVISION**

**CLEVITE CORPORATION**  
**CLEVELAND, OHIO**

Date: October 24, 1963

Project: 3 0 3 1 6 0

Copy No. 41

STUDY OF THIN FILM LARGE AREA

PHOTOVOLTAIC SOLAR ENERGY CONVERTER

*Fourth ...*

Fourth Quarterly Report

July 1, 1963 - September 30, 1963

NASA Contract No. NAS7-203  
National Aeronautics and Space Administration  
Western Operations Office

*(NASA CR-55740) DTS:\**

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# ABSTRACT

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This Fourth Quarterly Report discussed the work performed under Contract NAS7-203 during the period July 1, 1963, through September 30, 1963.

The effort expended on CdS solar cells during this quarter <sup>auth.</sup> has been devoted to obtaining reproducible films and cells. Thirty evaporations were completed yielding 237 films on glass substrates and two films on copper foil substrates. Improvements in the evaporation and standardization of the evaporation process resulted in "standard" films with quite uniform electrical properties. Cells processed from these films had efficiencies in the range 1.5 to 2.4 percent. Efficiency measurements made indoors are within 9 percent of those made in natural sunlight. A rather lengthy table is presented listing electrical properties and conversion efficiencies for a large number of photovoltaic cells.

The particle size and crystallite orientation, determined from x-ray studies, are presented. The topography of the film surface at each step of cell processing has been observed with the electron microscope. Electron micrographs are presented and discussed.

A summary of the "wet chemistry" approach to CdS film deposition is given for the last two quarters. *Author*

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1. INTRODUCTION

Present day photovoltaic solar energy converters are made of many small silicon cells, each of which must be soldered into a series-parallel array to provide the required electrical power for a given satellite system. A typical silicon cell is approximately 1 cm x 2 cm x 0.05 cm in size and has an efficiency of ten or fifteen percent; therefore, each cell delivers twenty or thirty milliwatts of power and many cells are required to power a satellite. Furthermore, each cell is very much thicker than its p-n junction; consequently, unnecessary weight is involved in a silicon solar cell array.

It is the purpose of this contract to develop a large area thin film photovoltaic solar energy converter. It is hoped eventually that cadmium sulfide cells one foot square and one or two mils thick will be produced, although for the present smaller areas will be studied. The highest efficiency of presently available thin film cadmium sulfide cells is around three percent over relatively small areas, and although the density of cadmium sulfide is twice that of silicon, the thickness of a cadmium sulfide cell is only about one-tenth that of a silicon cell. Thus, large area cadmium sulfide cells would compare favorably on a weight-per-watt and cost-per-watt basis with silicon cells. Furthermore, cadmium sulfide film cells have been produced on flexible metal and high-temperature organic plastic substrates, representing a great potential improvement over the rigid backing required by single crystal silicon cells.

This report covers work done during the fourth quarter of this contract.

2. EVAPORATED FILM CELLS

The effort expended on CdS solar cells this quarter has been devoted to obtaining reproducible films and cells. Thirty evaporations were completed

during the quarter yielding 237 films on glass substrates and two films on copper foil substrates.

Use of the quartz cloth screen permits evaporation of powder charges instead of crystal charges. This has led to a significant increase in reproducibility of electrical and photovoltaic properties of the CdS films.

Of the thirty evaporations completed this quarter, the first five were required to establish the new parameters resulting from the introduction of the quartz cloth screen; the last two were experimental depositions on copper foil substrates. The intervening 23 evaporations were standard "production" runs of which 17 produced cells with efficiencies between 1.5 percent and 2.5 percent, 5 yielded cells with efficiencies less than 1.5 percent but greater than 1.0 percent and one evaporation was lost due to an improperly cleaned substrate.

Cell efficiencies were measured indoors and outdoors. The maximum discrepancy between any of the indoor-outdoor measurements was 9 percent; most measurements agreed within 5 percent.

## 2.1 Evaporator

The quartz cloth screen is quite successful. Finely ground powders are being evaporated without any spattering whatever. This permits close control over the evaporant and elimination of the expensive practice of evaporating single crystal chips.

During evaporations 39 and 40, it was observed that the heater coil tended to sag when hot, causing a change in the spacing between turns. This left fewer turns per inch at the top of the crucible than at the bottom resulting in a change in temperature gradient along the crucible. Since evaporation essentially takes place from the quartz cloth screen, this meant that the actual evaporation temperature was lower, resulting in a change in film resistance. The problem was solved by using slotted ceramic spacers to maintain the heater coil geometry. The spacers have since been eliminated by stuffing the space around the coil with a fibrous refractory. The heater is now a 14 turn, 3/4-inch I.D. tantalum coil which has its top three turns spaced 1/32-inch apart while the remainder are uniformly spaced 3/32-inch apart. In the closely wound section, the temperature is highest. This arrangement

gives a very high evaporation rate; a layer  $2.5 \times 10^{-3}$  cm thick requiring only five minutes of evaporation contrasted with twenty minutes using the uniformly spaced heating coil. Furthermore, this is accomplished without increasing the heater power.

The heated cylinder surrounding the evaporator and substrate was described in the Third Quarterly Report.<sup>(1)</sup> It is used in all evaporations and contributes greatly to the increased rate of deposition.

## 2.2 Evaporant

The charge for all evaporations is now a powder. Sometimes the powder is a mixture of doped and undoped CdS which must be sintered in place to insure proper distribution of the dopant. This is accomplished by heating the charge in the crucible at a moderate temperature for a few minutes immediately before evaporation. At other times the charge consists of a mixture of presintered boules which have been finely ground. Both methods provide uniform, easily controlled, predetermined doping levels in the charge.

Control of the evaporant has resulted in greater uniformity of electrical properties of the films. For example, in the last 12 evaporations, the doping level in the film was consistently maintained between 0.04 and 0.05 mol percent indium, whereas in earlier evaporations, the doping level might change by a factor of 10 or 100 between successive evaporations.

## 3. PROCESSING OF FILMS

The average efficiency of the film cells has been doubled by modifying the processing procedure slightly. In the past, copper oxide slurry was applied to the film at room temperature and dried at  $80^{\circ}\text{C}$  on a hot plate before the final  $300^{\circ}\text{C}$  heat treatment. Now, the slurry is put on the film after the film temperature has been raised to  $100^{\circ}\text{C}$ . After the slurry has dried completely, it is removed and the film is transferred to the  $300^{\circ}\text{C}$  hot plate for final heat treatment.

Experiments to improve cell quality are continuing. The presently established "standard" procedure regularly results in cells having efficiencies

of 1.5 to 2.0 percent. Active cell areas are generally 7 to 10 cm<sup>2</sup>. Typical properties of an "average" cell would be:

Open circuit voltage	0.41 volts
Short circuit current	54.0 milliamperes
Voltage at maximum power	0.27 volts
Current at maximum power	42.0 milliamperes
Active area	6.5 square centimeters
Light conversion efficiency	1.7 percent

$$\text{Fill factor} = \frac{V_{mp} \times I_{mp}}{O.C.V. \times S.C.C.} \quad 0.51$$

Illumination 100.00 mW/cm<sup>2</sup>

Cell parameters being given particular attention are open circuit voltage, short circuit current, and rectification.

It has been shown that the open circuit voltage increases if the resistivity of the film is increased by reducing the doping level. On the other hand, increased resistivity leads to higher series resistance in the inert layer of CdS. In an attempt to lower the series resistance, a coarse silver grid (1"x1") was evaporated onto a substrate before the CdS deposition. Cadmium sulfide was evaporated in the usual manner onto the striped substrate. Subsequent processing indicated no change in efficiency as a result of the evaporated silver conductors. The efficiency measured with the silver conductors in contact but beneath the cadmium sulfide layer was the same as the efficiency measured with the "standard" indium electrode placed around the perimeter on top of the cadmium sulfide layer.

In an experiment to increase the open circuit voltage while maintaining a low series resistance, a graded film was deposited. A doping level gradient was established by varying the doping level of the charge. Photovoltaic cells made in this manner were not greatly different from cells made from standard films.

The next attempt was to evaporate two distinctly separate layers in two separate evaporations. The layer from the first evaporation was made low in resistivity by vaporizing cadmium sulfide doped with 0.1 mol percent indium sulfide. Atop this layer a second layer of high resistivity undoped cadmium sulfide was deposited. Cells made from this double layer construction proved encouraging in the direction of increased open circuit voltages. A 1.2 percent efficient double layer cell displayed an open circuit voltage of 0.49 volts.

The lesser efficiency than the "standard" cells is in a large measure attributable to the thickness (0.5 mil) of the high resistance layer. An improvement in efficiency is anticipated if this layer is reduced to a thickness no greater than that consistent with continuity -- less than 0.1 mil.

A double layer CdS evaporation was also made onto a copper foil specimen treated in  $(\text{NH}_4)_2\text{S}$ . The ammonium sulfide treatment converted the  $\text{Cu}_2\text{O}$  side of the foil to  $\text{Cu}_2\text{S}$ . In this double evaporation experiment the first deposited layer was undoped cadmium sulfide and the second layer was highly doped (high conductivity) cadmium sulfide -- still maintaining the backwall construction. The deposition was carried out at a foil temperature of  $100^\circ\text{C}$ . The resulting deposit was poorly adherent, a condition not previously encountered with copper foil. No photoactivity was noted.

A cold two layer deposition of CdS on untreated Clevite copper foil should produce good photovoltaic activity. Alternatively, a single, thin, high resistance layer of CdS deposited on the  $\text{Cu}_2\text{O}$  layer of the foil followed with a low resistance metal grid should produce equivalent or better results than the two layer cadmium sulfide construction. In the latter method the metal grid replaces the low resistance CdS layer. The high resistance layer is to produce maximum open circuit voltages and its thinness combined with the metal grid is to reduce the series resistance to a minimum.

In view of the uniformity of electrical properties and the nonuniformity of efficiencies, it is very likely that the barrier layer formation now represents the next major obstacle to obtaining consistently good cells. This problem will be vigorously attacked in coming months. There are still many improvements to be made in the evaporation process but these will probably not contribute as significant an increase in cell efficiency as, say, an increase by one-third in rectification.

#### 4. MEASUREMENTS

One film from each evaporation was used for x-ray particle size determination and another for Hall effect and resistivity measurements. Most of the remaining films were processed into photovoltaic cells. Data obtained from these measurements are given in Table 4-1. A number of trends and observations, requiring further consideration, are discernable from these data. These are:

TABLE 4-1. PROPERTIES OF CdS PHOTOVOLTAIC FILM CELLS

[illegible]





TABLE 4-1. PROPERTIES OF CdS PHOTOVOLTAIC FILM CELLS (continued)

[illegible]

1. Most of the higher efficiency cells (efficiency  $> 1.5\%$ ) have x-ray determined particle sizes in the  $10 \text{ \AA}$  to  $15 \text{ \AA}$  range.
2. The efficiency of a cell does not appear to depend very strongly on carrier mobility.
3. High efficiency cells are obtained from films having higher electrical resistivity (mentioned in previous reports).
4. Higher efficiency cells have carrier concentrations in the range  $0.5 \times 10^{19}$  to  $1.0 \times 10^{19} \text{ cm}^{-3}$ .
5. High open circuit voltage almost always indicates a high efficiency cell.
6. Some cells show a rather large initial deterioration occurring within the first hour or two after processing. The rate of deterioration decreases rapidly thereafter.

The resistivity and Hall coefficients were measured in the usual manner and the mobility and carrier concentration calculated from these data as shown in Table 4-1. The data for the column labeled "indium concentration of film, mol percent" are calculated from the carrier concentrations assuming a one to one correspondence between the charge carriers and the indium impurity atoms. It is further assumed that the impurities are completely ionized at room temperature. While neither of these assumptions is entirely justified (the contribution of excess cadmium to the charge concentration is ignored) these calculated indium concentrations agree fairly well with the known indium concentration of the charge.

The efficiencies given in Table 4-1 were obtained from indoor and outdoor measurements. The agreement between these measurements is generally within 9 percent. Typical data are shown in Table 4-2. Also shown in the table are typical effects of deterioration observed when a considerable time lag exists between measurements.

TABLE 4-2. COMPARISON OF INDOOR AND OUTDOOR EFFICIENCY MEASUREMENTS.

Cell No.	Artificial Light Efficiency	Time Lag or Lead Between Measurements	Sunlight Efficiency	Area, cm <sup>2</sup>
37-4	0.6	Measured 14 days <u>after</u> sunlight measurement	0.8	8.0
46-5	2.5	Measured 4 days <u>before</u> sunlight measurement	2.1	1.5
49-3	1.4	10 minutes between indoor and outdoor measurements	1.4	9.9
49-5	1.7	10 minutes between indoor and outdoor measurements	1.6	8.8
49-8	2.4	10 minutes between indoor and outdoor measurements	2.2	2.8

A pair of evaporated films of contrasting (x-ray measured) particle size was selected for detailed study at each stage of the process for fabricating photovoltaic cells. The study includes observation of pole figure changes and electron microscopy of the surface by replication. The pole-figure curves show that no change in orientation takes place. Previously described experiments show that finite but small increases are affected in "particle size" by the heat treatments. This experiment is discussed in detail in Section 5.

In another experiment, two films were treated with cadmium vapor. One film, 20-1 was a very high resistance film from an early evaporation. It was heated to 600°C within one hour in an argon filled quartz tube containing a small piece of Cd metal. On cooling, the film split and detached from the substrate. The second film, 35-5 was treated similarly but heated very slowly, three hours to attain 400°C, and held for 30 minutes. This film remained intact and its resistivity and Hall coefficient were measured. Data taken before and after the Cd treatment show that the carrier concentration increased by about 300 times while mobility decreased by about 26 times.

It is interesting to compare semilog plots of the experimentally obtained voltage-current characteristics of CdS photovoltaic cells with those of various ideal photovoltaic cells. A number of the ideal models is being investigated in this fashion. The plots are quite tedious to calculate, however, and the work has not progressed sufficiently to warrant inclusion here. It is expected

that a full discussion will be ready in time for the next quarterly report.

## 5. FILM STRUCTURE STUDIES

### 5.1 Electron Microscope Studies

Electron micrographs show that the surface topography of CdS films is not visibly affected by the usual short heat treatments employed in processing. In one experiment, film 30-1-F was heated for 6 hours at 400°C in an argon atmosphere. Replicas of the film taken before and after the heat treatment show no significant topographical changes.

A pair of evaporated films of contrasting (x-ray measured) "particle size" was selected for careful study at each stage in the process of fabricating photovoltaic junctions. The study included observation of pole figure changes and electron microscopy of the surface by replication. The pole figure curves showed that no change in orientation takes place; previously described experiments showed that small but finite increases are affected in "particle size" by the heating steps.

The two samples selected were film 23-3-B which had a larger than usual "particle size" of  $41\text{\AA}$  and film 24-2 having a smaller than usual "particle size" of  $7\text{\AA}$ . Replicas of the same general areas of the same film samples were made: 1) after evaporation, 2) after etching with HCl, 3) after applying the copper slurry, and 4) after the final heat treatment of the photovoltaic cell.

Micrographs of 23-3-B, Fig. 5-1, show concentric steps having hexagonal symmetry; the areas are 1 to 5 microns across. Qualitatively this corresponds to the larger x-ray "particle size," but quantitatively they are about 1000 times larger. The hexagonal orientation, of course, corresponds to the observation from x-ray pole figures that the c-axes of the crystallites are not far from being perpendicular to the surface.

After etching 23-3-B, Fig. 5-2 shows large hexagonal pits having diameters of about 0.5 microns. Application of the copper slurry resulted in a softening of detail as shown in Figs. 5-3 and 5-4. Heat treatment for photovoltage produced no further change in appearance. Figures 5-5 and 5-6 are stereo pairs showing 23-3-B before and after etching with HCl.



Figure 5 - 1. Film 23-3-B as Evaporated



Figure 5 - 2. Film 23-3-B After HCl Etch





Figure 5 - 3. Film 23-3-B After HCl Etch and Application of  $\text{Cu}_2\text{O}$  Slurry



Figure 5 - 4. Another Area of 23-3-B Showing Locally  
Thinner Coating of  $\text{Cu}_2\text{O}$  Slurry

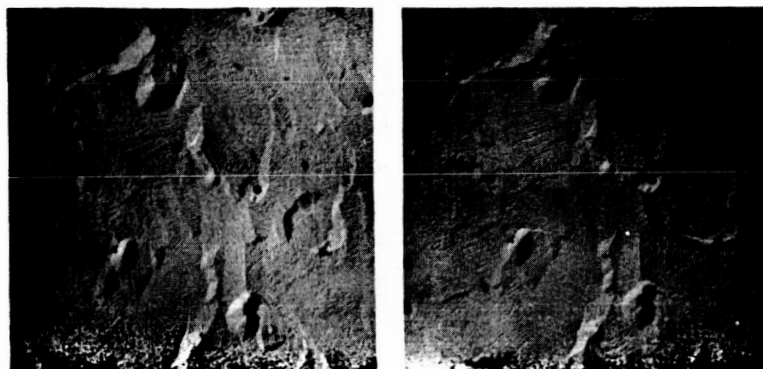


Figure 5 - 5. Stereo Pair of 23-3-B as Evaporated

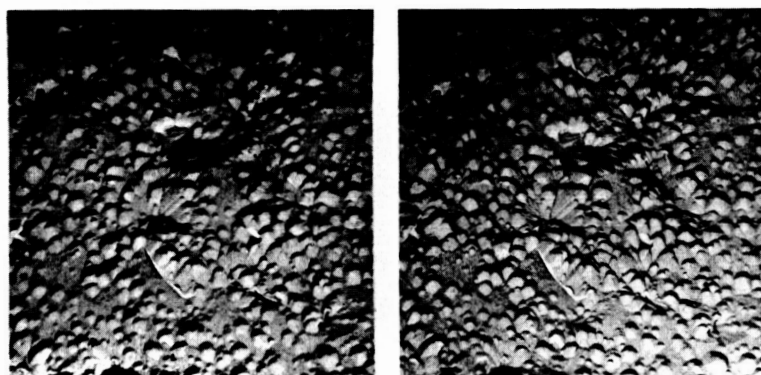


Figure 5 - 6. Stereo Pair of 23-3-B After HCl Etch

Film 24-2 initially appears (Fig. 5-7) as a "sandy desert from 5000 feet, winds prevailing from one direction." Etching produced a much coarser system of etch pits than expected from the small x-ray "particle size," the pits having a diameter of about 0.05 micron as shown in Fig. 5-8. This is about one-tenth the size of the pits in Film 23-3-B, proportionate to the x-ray measurements. Coating with copper slurry and heat treatment produced only insignificant changes in surface appearance, Fig. 5-9.

The hexagonal patterns described above are not those outlines observed on both glass and film surfaces and mentioned in previous reports. These latter outlines were originally found in electron micrographs of CdS films and subsequently found in electron micrographs of several varieties of glass as well as a polished quartz plate. It is concluded that they are artifacts, most likely introduced by the formvar.

## 5.2 X-ray Studies

### 5.2.1 Pole Figure Determination

The pole figure camera attachment for the x-ray diffractometer was completed. It operates satisfactorily and no unexpected difficulties have been experienced.

It has been noted in previous reports that the crystallites in CdS vacuum evaporated films tend to have their c-axes oriented nearly perpendicular to the substrate surface. In order to determine the magnitude of departure from perpendicularity, and the distribution of c-axis orientations, one would ordinarily use Bragg reflections from planes perpendicular to the c-axis. However, the only usable reflections are those from (002) planes for which the available observation angle ( $2\theta$ ) on a substrate opaque to x-rays is  $26.5^\circ$ . Thus, if the departure from perpendicularity of the preferred orientations of the c-axes is more than about  $13^\circ$ , it could not be measured directly, inasmuch as either the incident or reflected x-ray beam would lie inside the substrate.

Ordinary diffractometer measurements show anomalously high reflected intensities from the (10 $\bar{l}$ ) planes in evaporated CdS films, particularly from the (105), (106) and (107) planes. If one assumes that there is no preferred orientation of the a-axes (other than that imposed by the c-axis orientation) then one would expect the pole-figure diagram, for a



Figure 5 - 7. Film 24-2 as Evaporated



Figure 5 - 8. Film 24-2 After HCl Etch





Figure 5 - 9. Film 24-2 After HCl Etch and Application of  $\text{Cu}_2\text{O}$  Slurry

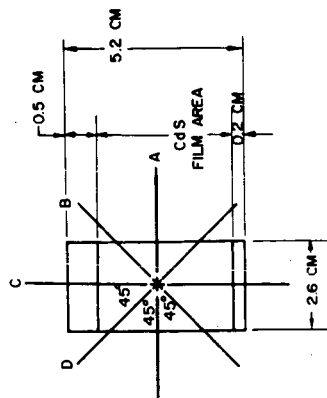


(10 $\ell$ ) plane in a polycrystalline configuration consisting of a single preferred c-direction, to be a ring with the c-axis pole for its center. This is indeed the situation observed on a large number of films using the pole-figure camera and reflection from the (107) planes. The pole vector of this plane is only 15° from the CdS c-axis while its 2 $\theta$  is about 112°. The ideal 2 $\theta$ , of course, would be 180°, but for evaporated films, it is observed that the farthest (107) reflections of appreciable intensity are seldom more than 30° or 40° from the substrate normal.

All raw data curves must be corrected for beam geometry effects: that is, truly random samples show a characteristic variation of reflected intensity as a function of incidence angle. The published theoretical curves for this effect do not exactly correspond to our experimental curves due, mainly, to differences in slit widths. The (107) diffraction intensity from a random CdS powder was found to be unusably weak, and therefore a calculation has been made to formulate a proper equation for our Norelco diffractometer geometry. These intensity corrections are rather substantial but have been verified by experiments with gold powder, establishing the validity of the inferred 2 $\theta$  random curve being used for the CdS (107) reflections.

The axis of rotation of the camera attachment lies in the plane of the film surface. If the c-axes have a preferred orientation peaking less than 15° from the rotation plane (of the incident and reflected x-ray beams), there will be two (107) intensity maxima observed during the sample rotation. When the sample is reoriented by turning it through, say, 90° about its own surface normal, two more (107) maxima will be observed, providing the same 15° restriction holds. If the distance in degrees of each (107) maximum from the sample's surface normal is plotted in the proper azimuthal direction the four points are found to lie on a circle whose radius is 15° and whose center corresponds to the location of the preferred c-axes direction. If the sample orientation is chosen so that the rotation plane does not intersect two (107) maxima, a single weak peak is ordinarily found; additional orientations can then be run to obtain sufficient points on the (107) circle.

Fig. 5-10 shows a contour map of (107) x-ray intensity for sample 36-2-A. Two 45° traverses were made to confirm the two 90° traverses; the contours are sketched in to illustrate a typical intensity distribution.



DIMENSIONS OF SAMPLE AND ORIENTATION WITH RESPECT TO X-RAY ROTATION TRAVERSES.

AREA EXAMINED APPROX. 1 CM<sup>2</sup> AT APPROXIMATE CENTER OF CdS FILM AREA. CONTOUR LINE ELEVATIONS REPRESENT CORRECTED RELATIVE X-RAY REFLECTION INTENSITIES OF (107). SOLID CIRCLES ARE EXPERIMENTAL MAXIMA. DASHED CONTOURS ARE INFERRED.

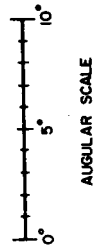
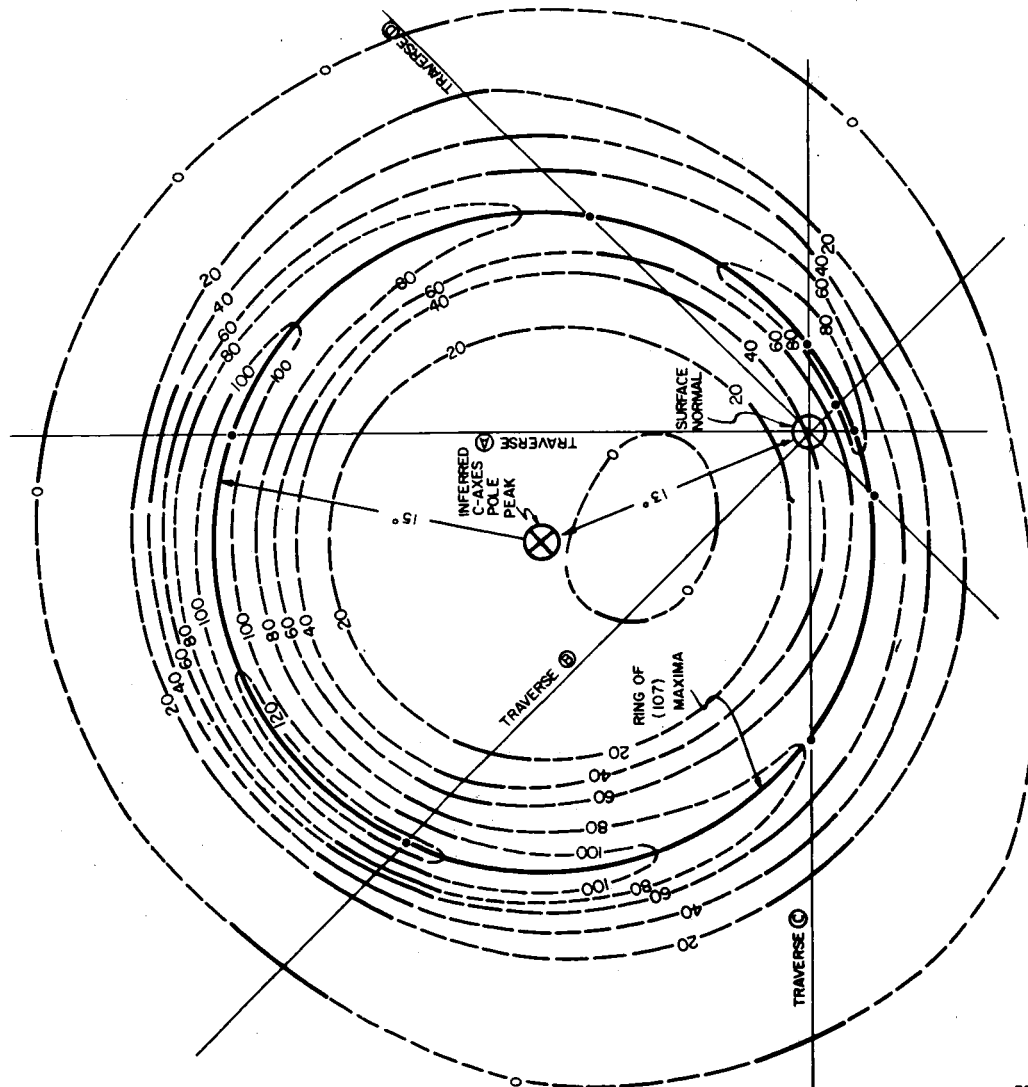


FIG. 5-10  
SAMPLE 36-2-A  
POLE FIGURE OF (107) X-RAY  
REFLECTION INTENSITIES



Of the twelve determinations made so far, most showed excellent parallelism between the (00 $\ell$ ) planes and the glass substrate surface; one had its z-axis maximum 2° from the CdS film surface normal while the others had values ranging from 12° to 19°. In most cases the observed (107) maxima were sufficiently sharp that the resultant locations of the z-axes preferred orientations are in error by less than one degree.

Table 5-1 summarizes these results. Significant correlations with other properties have not yet been observed.

#### 5.2.2 X-ray Determined Particle Size

Nominal particle sizes for evaporated CdS films have been obtained from measurements on x-ray line width broadening. This has been done for at least one film from nearly all of the evaporations conducted thus far. The results are tabulated in Table 5-2 below.

### 6. ALTERNATE METHODS OF PRODUCING CdS FILMS

The primary objective of this phase of the program was to deposit cadmium sulfide films on substrates by methods different from the vacuum evaporation technique. Two principal approaches were followed: an electroless plating process which had been successful in the deposition of lead sulfide mirrors and a sintering process based on the Thomsen patent<sup>(2)</sup> which had been successful in the fabrication of CdS photoconductive cells. Some of this work was described in detail in the appendix to the Third Quarterly Report<sup>(1)</sup> and the rest will be described in the following subsection. All the sintering processes studied require temperatures up to 600°C for successful deposition of CdS layers. Lower temperature sintering processes have not been found in the literature, nor were any discovered in the course of this preliminary experimental work. Consequently, all efforts under this phase have been channeled into a search for: 1) a process of depositing a CdS mirror, at temperatures less than 400°C, on duPont H-Film; and 2) a means whereby the H-Film may be treated to improve the bonding between it and a vacuum evaporated CdS film.

#### 6.1 Sintering Experiments on Glass

Most experiments were based on Thomsen's Patent. This utilizes

TABLE 5-1. ANGULAR ORIENTATION OF CRYSTALLITE Z-AXES WITH  
RESPECT TO SURFACE NORMAL FOR CdS EVAPORATED FILMS

Sample No.	Angle of Z-axis maximum with respect Surface Normal
18-3-D (end of plate directly over evaporator)	16°
18-3-D (center of plate)	17°
18-3-D (end of plate farthest from evaporator)	19°
21-3-F	17.5°
23-3-B (See Figs. 5-1 through 5-6)	12°
24-2 (See Figs. 5-7 through 5-9)	13.5°
30-BB	2°
31-2-B	13°
33-1-G	13.5°
34-2-C	12°
36-2-A	13°
37-7	13.5°
39-8	16.5°

TABLE 5-2. CRYSTALLITE SIZE DETERMINED FROM X-RAY DATA

Specimen No.	Nominal Particle Size (Å)	Specimen No.	Nominal Particle Size (Å)
CdS Powder, G.E.	22.8 (average)	38-4	15.8
16-3-H*	16.1	39-8	41.9
16-3-C	17.3	40-2	28.9
18-3-D	17.0	41-4	9.8
19-1	11.3	42-5	8.8
20-7	7.9	43-4	12.1
21-3-F	10.8	44-1	13.8
23-3-B	41.2	45-8	13.4
24-2*	7.2	46-2	15.5
25-1-C	17.6	47-8	9.8
27-1-H	18.7	48-7	10.0
28-AA	11.2	49-2	15.5
29-2-B	29.1	50-1	17.0
30-BB	28.5	51-7	24.0
30-1-G	17.8	52-7	14.6
32-AA	10.5	53-7	16.8
33-1-G	8.8	54-8	17.0
34-2-C	12.2	55-8	17.0
36-2-C	12.2	56-1	16.4
37-7	25.4	57-7	14.9
		58-5	7.9
		59-5	7.6
		60-7	15.8

\*After etching 5 sec. 1:1 HCl.

the fact that CdS dissolves in molten CdCl<sub>2</sub>. At a temperature of 400-600°C, CdCl<sub>2</sub> evaporates, leaving on the substrate a firmly adhering layer of interlocked CdS crystallites. Work began with Pyrex glass substrates. Later, investigations were extended to the use of copper foil substrates which possessed two desirable properties: light weight and flexibility. Emphasis was placed on obtaining firm bonding between film and substrate rather than aiming for photovoltaic effect since the latter could be achieved by suitable doping of the CdS. For this reason impurity contents of the materials are not listed.

Investigations were pursued in several directions, particularly in reference to compounding of the film and method of its application. Slurries consisted of doped or undoped CdS powder dispersed in water, and mixed in plastic jars with burundum stones, on ball mill rollers. Application of the CdS to the substrates included spraying, screening, brushing, rolling (with a 1/4" metal pin) and smearing. The films were dried at 105°C and then sintered at temperatures up to 600°C. The CdCl<sub>2</sub> flux volatilizes at temperatures above 400°C and at 600°C volatilization is complete while that of CdS is negligible. Whenever film resistance measurements were taken the indium tipped probes were about 5mm apart.

A heavy slurry containing doped CdS and 10 wt % CdCl<sub>2</sub> (based on CdS) was brushed on several pyrex plates. The remaining slurry was then thinned with water and a few more plates were prepared by brushing. The films were sintered at 600°C with 10 mins. holding time in an argon atmosphere.

The heavy slurry produced thick, well adhering, orange-yellow films of uneven thickness. There were a few scattered reddish areas, the cause of which is unknown. Resistances ranged between 10<sup>5</sup> and 10<sup>6</sup> ohms.

The thin slurry resulted in thin films with many pinholes, but otherwise similar in appearance to the films described above. Resistances measured from 10<sup>3</sup> to 10<sup>4</sup> ohms.

In attempts to form layers of doped cadmium sulfide, the following experiments were performed:

- 1) CdS powder, 10 wt.-% CdCl<sub>2</sub> and 0.1 mole % InCl<sub>3</sub> were made into a thin slurry and brushed on to several pyrex plates. Sintering was carried out in argon at 600°C with 10 mins. holding time. The films cracked and did not adhere at all well.

2) A mixture was made of CdS powder, 0.05 mole %  $\text{In}_2\text{S}_3$  powder, 10 wt. %  $\text{CdCl}_2$  and enough water to render a moderately heavy slurry. This was applied to a few plates by screening, and to some more by rolling and smearing. The remainder of the slurry was thinned down and used for spraying.

The screened films which were sintered in air at  $600^\circ\text{C}$  with 5 mins. holding time adhered well but were uneven in thickness. They were of yellow color with a few scattered reddish "islands." Resistances were of the order of  $10^6$  ohms.

The rolled-on and smeared-on films were sintered in argon with 90 mins. holding at  $550^\circ\text{C}$ . Adherence was satisfactory, but the films again had varying thicknesses (0.06 to 0.14 mm). Resistances measured  $10^4$  to  $10^6$  ohms. The rolled-on films exhibited numerous very short cracks.

The sprayed films sintered in argon and held at  $600^\circ\text{C}$  for 30 mins. adhered poorly.

3) A charge consisting of thoroughly mixed powders of CdS and 0.4 mole %  $\text{In}_2\text{S}_3$  was sintered at  $800^\circ\text{C}$  in a covered alumina crucible. The resulting cake was found covered with a thin crust of black crystallites which were identified by x-ray as CdO. After removal of this crust, a weighed amount of the innermost core of the cake was wet ground with 10%  $\text{CdCl}_2$ , 5% aqueous solution of 1:1 ceramul wax and 100% distilled  $\text{H}_2\text{O}$ . It was hoped that the wax in the thin slurry would keep the CdS particles in suspension for a reasonable length of time. After spraying, the films were sintered in argon at  $600^\circ\text{C}$  for 7 mins. Adherence was very good. Again there were scattered red spots which this time were only pin head size. Resistances were in the  $10^5$  ohm range.

It was conceivable that the high film resistances were caused by loss of Cd during sintering. For this reason one sample was reheated to  $600^\circ\text{C}$  in the presence of Cd vapor. The resistance dropped to 1000-2000 ohms but no photovoltaic activity could be detected. Another sample treated similarly with a mixture of Cd-Ga vapors exhibited a weak photovoltaic effect.

The above experiments lead to the conclusion that spraying and screening are feasible techniques for applying CdS films to glass substrates. The quick settling of the heavy CdS particles from an aqueous slurry necessitated frequent stirring, and this caused spraying with interruptions. The sintered films, though bonding well, had a mottled appearance due to aggregation of the solid particles. These problems do not seem to be serious and could be solved by work leading to



a vehicle better than water, and to a suspending agent more effective than the ceramul wax.

Screening the heavy aqueous slurry does not produce a satisfactory film. It would be desirable to search for an "ink" which would permit the film to smooth out to an even and controlled thickness.

## 6.2 Sintering Experiments on Copper Foil

Experiments were carried out with foils covered with  $\text{Cu}_2\text{O}$  as well as with foils covered with  $\text{Cu}_2\text{S}$ . The presence of a thin layer of  $\text{Cu}_2\text{O}$ , on one side of the foil, which easily converted to the sulfide could be considered as a "bonus." The difference in coefficients of thermal expansion was notable: about  $17 \times 10^{-6}$  for the Cu and  $4 \times 10^{-6}$  for CdS. It was hoped that because of the thinness of the film and foil, this would not become a serious problem. Methods of applying the CdS films were the same as for glass substrates. In addition hot pressing was also tried.

CdS doped with 0.003 at. % In was produced by sintering thoroughly mixed powders of CdS doped with 0.1 at. % In (boule T-2) and undoped CdS at  $575^\circ\text{C}$  in argon. The resulting cake was ground to a fine powder.

For the first experiment a thin slurry was prepared. It consisted of a weighed amount of this powder, 10%  $\text{CdCl}_2$ , 5% ceramul wax solution (1:1) and sufficient water to produce the requisite consistency. The films had to be sprayed on to the substrate and dried (at  $105^\circ\text{C}$ ) repeatedly in succession to prevent them from "running" wet, and also to build up thickness.

Other films were produced on foils heated to  $380^\circ\text{C}$  on a hot plate. Immediate drying of the films permitted uninterrupted spraying in a single operation.

In the next experiment a syrupy ink consisting of the powdered CdS, 0.003 at. % In, 5%  $\text{CdCl}_2$  and glycerin was screened on to several foils.

All these samples were sintered in argon for 1 hour at  $535^\circ\text{C}$ . The films were found blistered and flaking off. Their color, originally yellow, turned partially or completely black; this was indicative of Cu having diffused into the film and displacing Cd.

Attempts were made to produce the CdS film in situ. One substrate was wetted with  $(\text{NH}_4)_2\text{S}$  solution and then sprayed with  $\text{CdCl}_2$  solution. Another

substrate was sprayed with  $\text{CdCl}_2$  solution and, after drying, wetted with  $(\text{NH}_4)_2\text{S}$  solution. The CdS films which formed were uneven, spotty and fell off readily on drying.

In the last experiments an effort was made to bond film and foil by hot-pressing. Circular substrates (0.93 inch dia.) were dusted with In doped (0.05 at. %) CdS powder using a 325 mesh screen, and then placed into the hot press preheated to  $250^\circ\text{C}$ ,  $400^\circ\text{C}$  and  $500^\circ\text{C}$ . The load on the pins was 16000 lbs. (24000 psi) each time. The samples were allowed to cool under pressure in order to prevent curling or dishing. At  $250^\circ$  and  $400^\circ$  the films remained powdery and fell off. At  $500^\circ\text{C}$  sintering did take place, but the sintered film also stuck in spots to the pin, even when an aluminum foil was used for separation. Examination of the undamaged parts of the sample revealed that diffusion of copper into the CdS film was extensive.

Because of the lack of bonding between the copper foil substrate and the CdS film and also because of the damaging migration of copper into the film, no further work with the copper foil is planned. except to prepare the surface for vacuum evaporation experiments.

## 7. WORK PLANNED FOR NEXT QUARTER

In the next quarter, the emphasis will be on: 1) improvement of the rectification characteristics of the CdS photovoltaic cells, 2) fabrication of cells on duPont H-Film, and 3) increasing open circuit voltage and short circuit current of cells deposited on glass substrates.

## 8. REFERENCES

1. W. J. Deshotels, et al., "Study of Thin Film Large Area Photo-Voltaic Solar Energy Converter," Third Quarterly Report, July 19, 1963, Contract No. NAS7-203.
2. S. M. Thomsen, "Sintered Photoconducting Layers," U. S. Patent 2,765, 385, October 2, 1956, (Assigned to Radio Corporation of America.

9. PERSONNEL

Time devoted to this project by principal technical personnel and others in the period July 1, through September 30, 1963, follows:

<u>Personnel</u>	<u>Hours</u>
W. J. Deshotels	452
F. Augustine	462
A. Carlson	186
J. Koenig	432
Others	<u>1825</u>
Total	3357 .

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